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Description

The present invention relates to glasses for ophthalmic applications which, in addition to the properties of ultraviolet radiation (UV) absorption and high transmission in the visible (absence of coloration), have a low density, as well as corrective lenses produced from these glasses.

These glasses are characterized by an index of refraction (n_d) of 1.523±0.004, an Abbe number (V_d) between 51—59, and a density (D) less than 2.43g/cm³. Their transmission at 400 nm is, for a thickness of 2 mm, greater than 89%. Their UV cutoff, defined as the wavelength for which the transmission is equal to 1% for a thickness of 2 mm, is between 325—335 nm. Moreover, they exhibit excellent chemical durability (A.O. test).

Lenses of inorganic glass ("white" or tinted) for ophthalmic use have, to a very great extent, an index of refraction n_d=1.523. The "white" (or tinted) glasses used at the present time and which exhibit in certain cases a UV cutoff higher than 300 nm, have a density at least equal to 2.54 g/cm³. A reduction of the density and, consequently, of the weight of the lens, offers an obvious advantage for the wearer and that regardless of the power of the lens. The lightening of the lens by the glasses of this invention is about 6.5—7%.

Summary of the invention

The glasses of the invention belong to the base system SiO_2—B_2O_3—TiO_2—R_2O (R=Li, Na, K) and are prepared from a batch composition consisting essentially in weight percent on the oxide basis of:

SiO_2	54—70	$Li_2O+Na_2O+K_2O$	10—13
B_2O_3	9—22	TiO_2	4—6
Al_2O_3	3—10	ZrO_2	0—2
Li_2O	0.5—3	As_2O_3	0.10—0.50
Na_2O	3—9	Cl	0.2—0.7
K_2O	3—10		

The content of SiO_2 lies between 54—70% approximately and results from the choice of the other glass components whose content limitations are described below.

B_2O_3 is an essential element of the glass because it especially makes it possible to obtain a low density; when B_2O_3 increases, the density of the glass decreases, the UV cutoff rises and the viscosity of the glass at high temperature decreases, which facilitates its melting and forming. To eliminate B_2O_3 from the glass would lead, on the one hand, to a density situated at the higher admissible limit, and, on the other hand, to higher melting and forming temperatures. Therefore, the glass will contain at least 9%. Above 26%, the SiO_2 content would have to be greatly reduced, thereby reducing the chemical resistance of the glass and the transmission.

Besides improving the chemical resistance, Al_2O_3 substituted for SiO_2 reduces the density and, more significantly, increases the UV cutoff.

TiO_2 is the determining elememt for the UV cutoff. Besides its indispensable presence for UV absorption, TiO_2 contributes to the refractive index. Depending upon the content thereof, the index is adjusted with the alkali metal oxides, the concentration of ZrO_2, and/or of the alkaline earth metal oxides and/or ZnO.

ZrO_2 is preferred over MgO, CaO, BaO or ZnO for adjusting the index when the alkali metal oxides do not suffice. With respect to the alkali metal oxides, the sum $Li_2O+Na_2O+K_2O$ will range between about 10—13 %. The maximum concentration of alkali metal oxides is determined principally by the density, the refractive index, and the chemical durability. The proportion of the alkali metal oxides is adjusted as a function of the amount of TiO_2, B_2O_3, and Al_2O_3 in order to obtain the best compromise of properties—facility of melting and forming.

In particular, when TiO_2 is greater than 4% in the presence of average amounts of Al_2O_3 and B_2O_3, the concentration of Li_2O will be maintained below 3%. Based upon weight percentages and in substitution with regard to SiO_2, the contribution to the index and to the density increases in the following order: K_2O, Na_2O, Li_2O. In general, the UV cutoff diminishes when the quantity of alkali metal oxides increases. To obtain the high cutoff (>325 nm), the total content is less than 13%.

When TiO_2 is greater than 3—3.5%, thus in the range of 4—6% the glass is found to be more sensitive to the melting conditions in the sense that coloration ("rose-orange") unacceptable to a glass called "white" can be observed in certain cases. This is probably linked to the presence of Ti^{+3} ions; reducing melting conditions will be avoided. To improve the stability with respect to variations in melting conditions or batch materials, and in order to obtain "white" glass regardless of the TiO_2 content and particularly at 5% TiO_2, which leads to a high UV cutoff, As_2O_3 is added in an amount of 0.10 to 0.50%.

As_2O_3 contributes to the fining of the glass. This fining agent is not however sufficient and chlorine (with or without bromine) is introduced into the batch materials in the form of chlorine (bromine) compounds such as chloride (bromide) of sodium or potassium. In view of the volatilization duruing the melting process, only a fraction of the batched quantity will be present in the final glass.

Prior art

United States Patent No. 2,454,607 discloses glasses designed for sealing to a nickel-iron alloy, the glasses having composition consisting, in weight percent on the oxide basis, of

B_2O_3	20—24	Na_2O	≥2
Al_2O_3	3—6	K_2O	≥2
TiO_2	2—5	Li_2O	7—12
ZrO_2	0.5—1.5	SiO_2	56—68

No mention is made of ophthalmic applications, of a high UV cutoff, or of a colorless glass. Moreover, the Li_2O content is much higher than can be tolerated in the subject invention.

United States Patent No. 4,224,074 describes glass frits suitable for decorating glass, glass-ceramic, and ceramic articles, the frits consisting essentially, in weight percent on the oxide basis, of

SiO_2	29—55	Na_2O	4—20
B_2O_3	7—31	Li_2O	0—7
Al_2O_3	2—8	Na_2O+Li_2O	6—24
ZrO_2	5—16	F	0.75—4

No mention is made of ophthalmic applications, of a high UV cutoff, or of a colorless glass. Moreover, fluoride is a required component, which element forms no part of the subject invention, and TiO_2 is merely an optional ingredient.

Chemical Abstracts, Vol. 92, No. 4, 28th January 1980, No. 27323u discloses a UV absorbing glass of the following composition:

SiO_2	69.0%	
Al_2O_3	4.5	
B_2O_3	10.5	
Na_2O	7.0	where $Li_2O+Na_2O+K_2O=9.0\%$
K_2O	2.0	
BaO	2.0	
TiO_2	3.0	
CeO_2	2.0	

One particular glass 1.2 mm in thickness has UV transmissivity of 0% at ~365 nm.

US—A—4,001,019 discloses, in Examples 6 and 7, base glasses which are reversibly light sensitive, having the following compositions, expressed in weight %

Example 6

SiO_2	54.2
B_2O_3	18.9
Al_2O_3	8.5
K_2O	8.2
Li_2O	1.8
BaO	1.0
TiO_2	5.3
ZrO_2	1.9
As_2O_3	0.1
Sb_2O_3	0.1

Example 7

SiO_2	51.2
B_2O_3	18.6
Al_2O_3	11.5
K_2O	8.2
Na_2O	0.7
Li_2O	1.8
BaO	1.0
TiO_2	4.9
ZrO_2	1.9
Sb_2O_3	0.2

Description of preferred embodiments

The invention is illustrated through the examples provided in the attached table. The compositions are given in batched weight percentages. The batch materials utilized (and notably the source of SiO_2) must be carefully selected in order to maintain a minimum amount of Fe_2O_3. As a matter of fact, Fe_2O_3 in too large a quantity (greater than about 100 PPM in the glass) leads to a yellow coloration. This coloration results from the known interaction between Fe_2O_3 and TiO_2. Particularly for SiO_2, one utilizes quartz wherein the Fe_2O_3 content is on the average less than 10 PPM (parts per million). The other principal batch materials that can be utilized are boric acid [$B(OH)_3$], boric anhydride, the carbonates of Li_2O, Na_2O, and K_2O, titanium oxide, zirconium oxide, or zircon.

At least 2% Na_2O or K_2O will be introduced in the form of nitrates in order to obtain oxidizing conditions during melting of the mixture of batch materials.

The examples of the invention were prepared from mixtures representing 100 grams to several kilograms of glass. Melting of the batch materials took place at 1250°—1350°C following which the temperature was raised to 1400°—1460°C for homogenizing and fining the glass. Pouring took place after cooling to a temperature allowing either the forming of a bar or the pressing of a disc. The corresponding viscosity ranged between 100—1000 poises (10—100 Pa · s). The total time of the operation was on the order of 3—7 hours. After forming, the glass was annealed at about 480°C with a cooling rate to ambient temperature of 60°C/hour; the properties were then determined.

Measurements of refractive index and Abbe number were carried out according to conventional methods (for n_d the yellow ray of He was used) on glasses having been cooled from 480°C to ambient temperature at the rate of 60°C/hour. Density was measured by the immersion method and expressed in g/cm^3.

The chemical resistance in acid medium was evaluated by the A.O. test described in the journal *Applied Optics, 7,* No. 5, page 847, May, 1968. It consists of determining the loss of weight of a polished sample immersed at 25°C for 10 minutes in a 10% by weight aqueous solution of HCl. The loss of weight is expressed in mg/cm^2.

The transmission curve was recorded at a thickness of 2 mm with the aid of a Hewlett-Packard spectrophotometer (type 8450A).

The glasses of the invention can be tinted for an ophthalmic application by using conventional colorants: transition metal oxides or rare earth oxides or other known colorant elements. The total content of these colorants will not generally exceed 2%.

The glasses of the invention can be strengthened according to current techniques of thermal or chemical tempering. In the latter case, the strengthening requires the replacement of a Na^+ and/or Li^+ ion in the glass by Na^+ and K^+ ions in a bath of molten nitrates, which implies that the glass does not contain K_2O as the only alkali metal oxide.

In order to obtain a UV cutoff equal to or higher than about 325 nm, the glasses will be prepared from a batch composition consisting essentially, in weight percent on the oxide basis:

SiO_2	54—70	$Li_2O+Na_2O+K_2O$	10—13
B_2O_3	9—22	TiO_2	4—6
Al_2O_3	3—10	ZrO_2	0—2
Li_2O	0.5—3	As_2O_3	0.10—0.50
Na_2O	3—9	Cl	0.2—0.7
K_2O	3—10		

As previously described, the TiO_2 content must be adjusted as a function of the Al_2O_3, B_2O_3, and alkali metal oxide contents in order to obtain a UV cutoff greater or equal to 325 nm (see table of examples). For example, a low content of Al_2O_3 and B_2O_3 must be associated with a high concentration of TiO_2.

The particularly preferred glasses, because of their excellent properties and their facility for melting and forming on an industrial scale, are prepared from a batch composition consisting essentially, in weight percent on the oxide basis:

SiO_2	56—62	$Li_2O+N_2O+K_2O$	10.5—12.5
B_2O_3	15—20	TiO_2	4.2—5.5
Al_2O_3	4—7.5	ZrO_2	0—1.5
Li_2O	1—2.5	As_2O_3	0.10—0.50
Na_2	3—7	Cl	0.2—0.7
K_2O	3—6		

The most especially preferred glass is that of Example 1. This glass has a low density (2.37 g/cm^3), a high UV cutoff (330 nm), and exhibits no coloration in the visible. Furthermore, it has excellent chemical durability (loss of weight in the A.O. test=0.004 mg/cm^2) and can be easily produced in a continuous melting unit. It can also be formed at a viscosity of 3000—6000 poises (300—600 Pa · s) with no problem of devitrification.

TABLE

	1	2	3	4	5	6	7
SiO_2	58.89	55.91	69.21	69.21	59.26	65.69	58.89
B_2O_3	17.28	20.26	9.94	6.96	22.38	15.12	13.53
Al_2O_3	6.19	6.19	3.21	6.19	1.23	2.21	9.94
Li_2O	1.8	2.4	1.8	1.8	1.81	1.79	2.4
Na_2O	4.09	4.09	4.09	4.09	6.11	4.07	4.09
K_2O	5.81	5.81	5.81	5.81	3.84	5.79	5.81
TiO_2	5.07	4.47	5.07	5.07	4.5	4.46	4.47
Cl	0.57	0.57	0.57	0.57	0.57	0.57	0.57
As_2O_3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
n_d	1.5231	1.5213	1.5255	1.5231	1.5259	1.5226	1.5227
V_d	53	54.7	54.1	53.7	55	55.3	53.94
D	2.37	2.36	2.41	2.40	2.42	2.39	2.38
% Trans. 400 nm	90.1	89.7	90.1	90.4	89.9	90.2	90
UVnm Cutoff	330	326	325	327	324	323	327

TABLE (Continued)

	8	9	10	11	12	13	14
SiO_2	63.58	58.9	58.91	56.33	62.13	64.35	64.35
B_2O_3	14.1	15.29	17.87	18.15	14.35	12.27	14.27
Al_2O_3	3.2	6.19	6.19	6.19	6.22	3.23	3.23
Li_2O	—	2.79	1.8	1.8	0.81	1.81	1.81
Na_2O	6.05	3.09	9.89	4.09	6.1	4.12	4.12
K_2O	5.78	8.79	—	5.81	3.83	5.85	5.85
MgO	—	—	—	—	—	4	—
CaO	—	—	—	—	—	—	2
ZnO	1.98	—	—	—	—	—	—
ZrO_2	—	—	—	4.99	—	—	—
TiO_2	4.45	4.08	4.47	2.07	5.69	3.5	3.5
Cl	0.56	0.57	0.57	0.57	0.57	0.57	0.57
As_2O_3	0.3	0.3	0.3	—	0.3	0.3	0.3
n_d	1.5191	1.5269	1.5266	1.5205	1.5212	1.5224	1.5241
V_d	54.6	55.3	54.1	57.1	51.8	57.2	56.4
D	2.40	2.41	2.40	2.39	2.37	2.41	2.41
% Trans. 400 nm	91.2	90.6	90.7	90.7	89.5	89.4	91.8
UVnm Cutoff	323	322	324	311	333	319	320

TABLE (Continued)

	15	16	17	18	19	20	21
SiO_2	64.35	58.89	57.43	57.19	62.89	56.68	51.08
B_2O_3	14.27	10.55	18.15	18.07	16.16	17.87	18.18
Al_2O_3	3.23	12.92	6.19	6.17	3.21	6.19	6.21
Li_2O	1.81	2.4	1.8	1.79	1.8	—	0.5
Na_2O	4.12	4.09	4.09	5.06	4.09	13.92	—
K_2O	5.85	5.81	5.81	5.78	5.81	—	18.68
ZnO	2	—	—	—	—	—	—
ZrO_2	—	—	2.98	2.97	1.99	—	—
TiO_2	3.5	4.47	2.98	2.97	3.48	4.47	4.48
Cl	0.57	0.57	0.57	—	0.57	0.57	0.57
As_2O_3	0.3	0.3	—	—	—	0.3	0.3
n_d	1.5200	1.5228	1.5203	1.5250	1.5221	1.5230	1.5195
V_d	55.8	53.7	55.8	56.8	56.5	54.1	54.3
D	2.40	2.39	2.38	2.42	2.39	2.42	2.38
% Trans. 400 nm	90	90.5	91	91.1	89.8	89.9	90.4
UVnm Cutoff	320	330	317	316	319	323	323

Claims

1. A glass for ophthalmic applications having a refractive index of 1.523±0.004, an Abbe number between 51—59, a density less than 2.43 g/cm³, a transmission at 400 nm in 2 mm thickness greater than 89%, and a UV cutoff between 325 nm—335 nm, characterized in that it is prepared from a batch composition consisting essentially, in weight percent on the oxide basis of:

SiO_2	54—70	$Li_2O+Na_2O+K_2O$	10—13
B_2O_3	9—22	TiO_2	4—6
Al_2O_3	3—10	ZrO_2	0—2
Li_2O	0.5—3	As_2O_3	0.10—0.50
Na_2O	3—9	Cl	0.2—0.7
K_2O	3—10		

2. A glass as claimed in claim 1 characterized in that it is prepared from a batch composition consisting essentially, in weight percent on the oxide basis, of:

SiO_2	56—62	$Li_2O+Na_2O+K_2O$	10.5—12.5
B_2O_3	15—20	TiO_2	4.2—5.5
Al_2O_3	4—7.5	ZrO_2	0—1.5
Li_2O	1—2.5	As_2O_3	0.10—0.50
Na_2O	3—7	Cl	0.2—0.7
K_2O	3—6		

3. A glass according to claim 2 characterized in that it is prepared from a batch composition consisting essentially, in weight percent on the oxide basis, of:

SiO_2	58.89	K_2O	5.81
B_2O_3	17.28	TiO_2	5.07
Al_2O_3	6.19	As_2O_3	0.3
Li_2O	1.8	Cl	0.57
Na_2O	4.09		

4. A glass according to any of claims 1 to 3 characterized in that it is tinted by up to 2% by weight relative to the weight of the glass of at least one colorant element.

Patentansprüche

1. Glas für ophthalmische Anwendungen mit einem Brechnungsindex von 1,523±0,004, einer Abbéschen Zahl zwischen 51—59, einer Dichte von weniger als 2,43 g/cm^3, einer Durchlässigkeit bei 400 nm in einer Dicke von 2 mm von mehr als 89% und einer UV-Grenz zwischen 325 nm—335 nm, dadurch gekennzeichnet, daß es aus einer Ansatzzusammensetzung hergestellt ist, die im wesentlichen in Gewichts-% auf Oxidbasis besteht aus:

SiO_2	54—70	$Li_2O+Na_2O+K_2O$	10—13
B_2O_3	9—22	TiO_2	4—6
Al_2O_3	3—10	ZrO_2	0—2
Li_2O	0,5—3	As_2O_3	0,10—0,50
Na_2O	3—9	Cl	0,2—0,7
K_2O	3—10		

2. Glas nach Anspruch 1, dadurch gekennzeichnet, daß es aus einer Ansatzzusammensetzung hergestellt ist, die im wesentlichen Gewichts-% auf Oxidbasis besteht aus:

SiO_2	56—62	$Li_2O+Na_2O+K_2O$	10,5—12,5
B_2O_3	15—20	TiO_2	4,2—5,5
Al_2O_3	4—7,5	ZrO_2	0—1,5
Li_2O	1—2,5	As_2O_3	0,10—0,50
Na_2O	3—7	Cl	0,2—0,7
K_2O	3—6		

3. Glas nach Anspruch 2, dadurch gekennzeichnet, daß es aus einer Ansatzzusammensetzung hergestellt ist, die im wesentlichen Gewichts-% auf Oxidbasis besteht aus:

SiO_2	58,89	K_2O	5,81
B_2O_3	17,28	TiO_2	5,07
Al_2O_3	6,19	As_2O_3	0,3
Li_2O	1,8	Cl	0,57
Na_2O	4,09		

4. Glas nach einem der Ansprüche 1—3, dadurch gekennzeichnet, daß es bis zu 2 Gewichts-% bezogen auf das Gewicht des Glases mit wenigstens einem Farbmittelelement getönt ist.

Revendications

1. Verre à usage ophtalmique, possédant un indice de réfraction de 1,523±0,004, un nombre d'Abbe compris entre 51 et 59, une densité inférieure à 2,43 (g/cm³), une transmission à 400 nm supérieure à 89 % sous une épaisseur de 2 mm et une absorption dans l'ultraviolet entre 325 et 335 nm, caractérisé en ce qu'il est préparé à partir d'une composition vitrifiable, contenant essentiellement les ingrédients ci-après, exprimés en oxydes (pourcentages en poids):

SiO_2	54—70	$Li_2O+Na_2O+K_2O$	10—13
B_2O_3	9—22	TiO_2	4—6
Al_2O_3	3—10	ZrO_2	0—2
Li_2O	0,5—3	As_2O_3	0,10—0,50
Na_2O	3—9	Cl	0,2—0,7
K_2O	3—10		

2. Verre suivant la revendication 1, caractérisé en ce qu'il est préparé à partir d'une composition contenant essentiellement les ingrédiznts ci-après, exprimés en oxydes (pourcentages en poids):

SiO_2	56—62	$Li_2O+Na_2O+K_2O$	10,5—12,5
B_2O_3	15—20	TiO_2	4—6
Al_2O_3	4—7,5	ZrO_2	0—2
Li_2O	1—2,5	As_2O_3	0,10—0,50
Na_2O	3—7	Cl	0,2—0,7
K_2O	3—6		

3. Verre suivant la revendication 2, caractérisé en ce qu'il est préparé à partir d'une composition contenant essentiellement les ingrédients ci-après, exprimés en oxydes (pourcentages en poids):

SiO_2	58,89	Na_2O	4,09	TiO_2	5,07
B_2O_3	17,28	K_2O	5,81	As_2O_3	0,3
Al_2O_3	6,19			Cl	0,57.
Li_2O	1,8				

4. Verre suivant l'une quelconque des revendications 1 à 3, caractérisé en ce qu'il est teint avec jusqu'à 2 % de son poids d'au moins un composé ou élément colorant.